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ATRAZINE RESIDUES IN NORTHERN OHIO 1980.(U)
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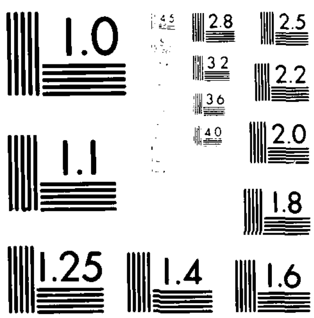

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Atrazine residues in water were measured periodically from mid-May to mid-July 1980 for eight sites in the Sandusky River basin and for fourteen other northern Ohio streams draining into Lake Erie. Concentrations in the Sandusky River varied from 1.0 - 45.7 ug/1. Atrazine was present at levels greater than 20 ug/1 in 12.5% of the samples and greater than 5 ug/1 in 63.9% of the samples. Concentrations in the other streams ranged from 0.1 - 23.2 ug/1 with 2.3% of the samples greater than 10 ug/1, 27.9% greater than cont

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5 ug/1 and 23.3% less than 1 ug/1. For several stations, atrazine levels were studied at more frequent intervals during a runoff event to observe variation with time and to attempt correlation with other parameters. Data for flow, suspended solids, and nitrates-nitrites are included for the Sandusky River samples and linear correlations between atrazine and each of these three parameters are discussed.

12

ATRAZINE RESIDUES IN NORTHERN OHIO STREAMS -- 1980

by

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September, 1980

This report is submitted in fulfillment of Contract DACW49-79-C-0020 from the U. S. Army Corps of Engineers, Lake Erie Wastewater Management Study, 1776 Niagara Street, Buffalo, New York 14207.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Atrazine residues in water were measured periodically from mid-May to mid-July 1980 for eight sites in the Sandusky River basin and for fourteen other northern Ohio streams draining into Lake Erie. Concentrations in the Sandusky River varied from 1.0 - 45.7 ug/l. Atrazine was present at levels greater than 20 ug/l in 12.5% of the samples and greater than 5 ug/l in 63.9% of the samples. Concentrations in the other streams ranged from 0.1 - 23.2 ug/l with 2.3% of the samples greater than 10 ug/l, 27.9% greater than 5 ug/l and 23.3% less than 1 ug/l. For several stations, atrazine levels were studied at more frequent intervals during a runoff event to observe variation with time and to attempt correlation with other parameters. Data for flow, suspended solids, and nitrates-nitrites are included for the Sandusky River samples and linear correlations between atrazine and each of these three parameters are discussed.

The discovery of the triazine herbicides in the 1950's has been characterized as a major breakthrough for agriculture, figuring greatly in improved corn yields. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has emerged in the 1970's as the most widely used herbicide in the United States (10).

As a moderately persistent herbicide, atrazine provides season long weed control in corn, sorghum, and several other crops. A period of 10 months is required for a 75 - 100% loss of atrazine from the soil after application (3). This fact suggests that atrazine has ample opportunity to reach area streams via surface runoff during the entire growing season. Atrazine's relatively high water solubility (33 ppm at 25 C) allows it to leach through the soil and into drainage tiles. In fact a number of studies (1, 7, 12, 13) document both routes, and atrazine has been detected in a variety of streams in Ontario and the Midwest (5, 6, 13).

In this work atrazine levels in 15 Ohio streams flowing into Lake Erie were studied. The Sandusky River and several of its tributaries, which were studied more extensively, should prove of particular interest, because the basin is located in a heavily agricultural area. During 1978, 363,700 acres or 75.8% of all corn acreage in the north central Ohio region, in which the Sandusky lies, was treated with atrazine. In the nearby northwest region, 417,600 acres or 56.8% of all corn acreage was treated with atrazine. Between 25 and 30% of the agricultural acreage in these two regions is planted in corn (2).

This report includes work performed under three different grants. The data reported in Table 2 were collected as part of a river transport research grant (R805436020) from the U.S. EPA. Data in Tables 3 and 5 were collected as part of Contract DACW49-79-C-0020 from the U.S. Army Corps of Engineers, Lake Erie Wastewater Management Study. The data in Table 4 were collected as part of a Lake Erie Tributary Loading Study (R005358-01) supported by the Great Lakes National Program Office of the U.S. EPA.

METHODS AND MATERIALS

FIELD SAMPLING

A variety of field sampling techniques were used in this study. For individual samples reported in Tables 2 and 3, grab samples of surface waters were collected by Heidelberg Water Quality Laboratory staff. Samples were placed in half gallon Mason jars with foil lined lids and refrigerated within eight hours of collection. These samples were all extracted within one week of collection. The composited samples reported in Tables 2 and 3 were obtained with automatic samplers (Isco Model 1680 or equivalent). Prior to compositing and extraction, the samples were held in plastic bottles in the sampler base for up to twelve days without refrigeration. Samples for the storm event data reported in Table 5 were also obtained with automatic samplers. The samples reported in Table 4 were collected by U. S. Geological Survey personnel using grab sampling techniques. These samples were stored in half gallon glass jars under

refrigeration for up to three weeks prior to extraction. Samples were taken from eight stations along the Sandusky River and its tributaries (Figure 1) from late May until mid-July, coinciding with the majority of the runoff events following spring planting. Fourteen other U.S. streams draining into Lake Erie were sampled on a less frequent schedule (Figure 2).

ANALYTICAL PROCEDURE

Analysis was performed according to the U.S. EPA method for triazine with only slight modifications (15). One liter of sample water was extracted with two successive 100 ml portions of methylene chloride. In a number of cases less than a liter of water was used with satisfactory results. Emulsions were broken by filtering through glass wool. The combined extracts were dried over sodium sulfate and concentrated using a Kuderna-Danish apparatus. After addition of hexane they were again concentrated and made up to a 10 ml volume with hexane.

The gas chromatograph was a Varian 3700 equipped with a thermionic specific detector and a Cole-Parmer integrating recorder. A 4 ft x 2 mm glass column packed with 5% Carbowax 20M on 80/100 Chromosorb W HP was used. The column was operated isothermally at 200 C, while the injector and detector were held at 250 C. The carrier gas was helium supplied at 30 ml/min. Hydrogen and air were supplied to the detector at flow rates of 4 and 290 ml/min., respectively. The bead current was 5.0 amps. Quantitation was possible down to approximately 0.05 ug/l. Fifty percent full scale deflection was given by 2 ng atrazine with a

Sampling Stations and
USGS Location Numbers

1. Bucyrus 04196000
2. Nevada 04196200
3. Mexico 04197000
4. Melmore 04197100
5. Upper Honey Creek 04197020
6. Wolf East 04197450
7. Wolf West 04197300
8. Tindall 04198000

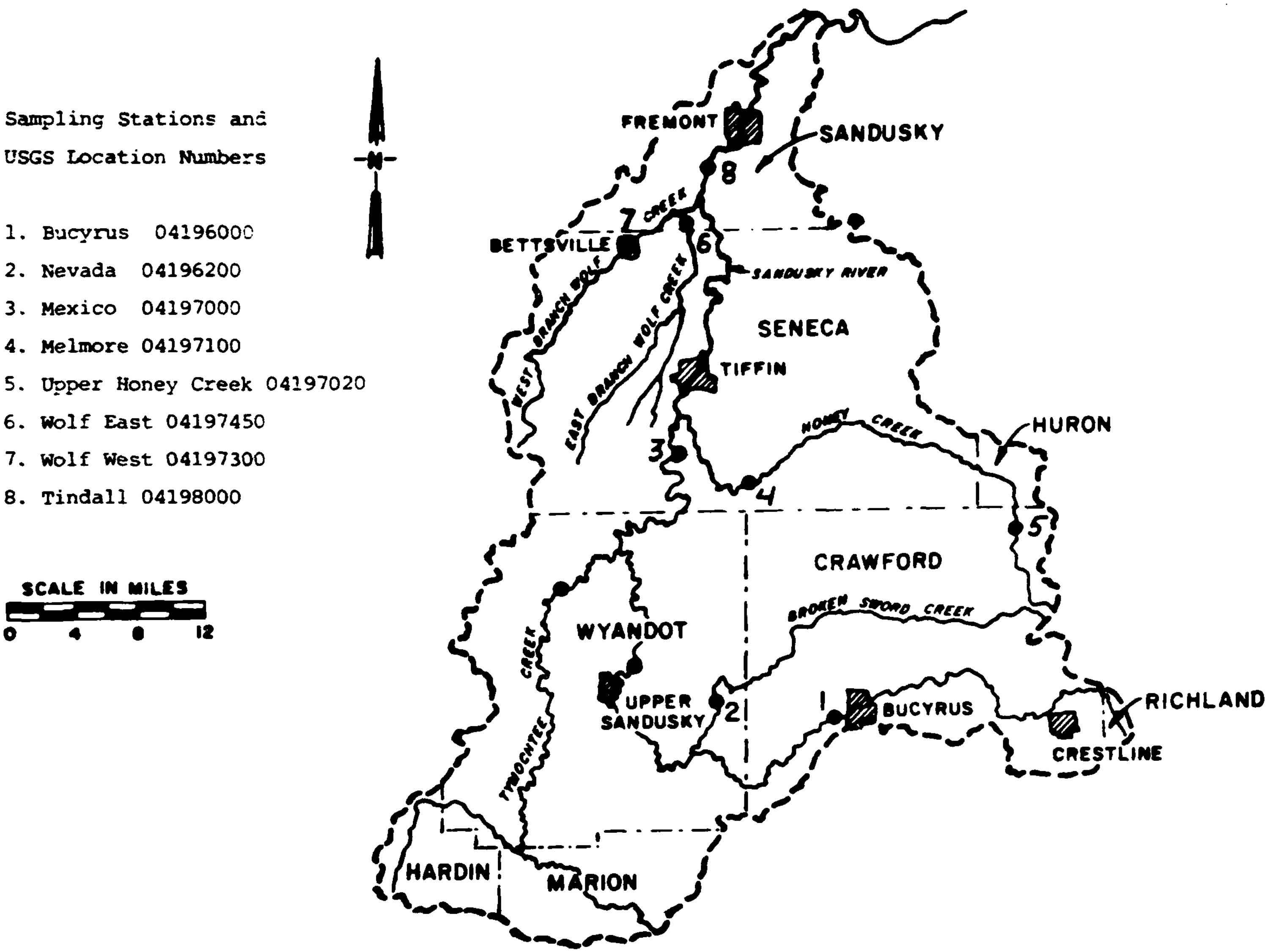
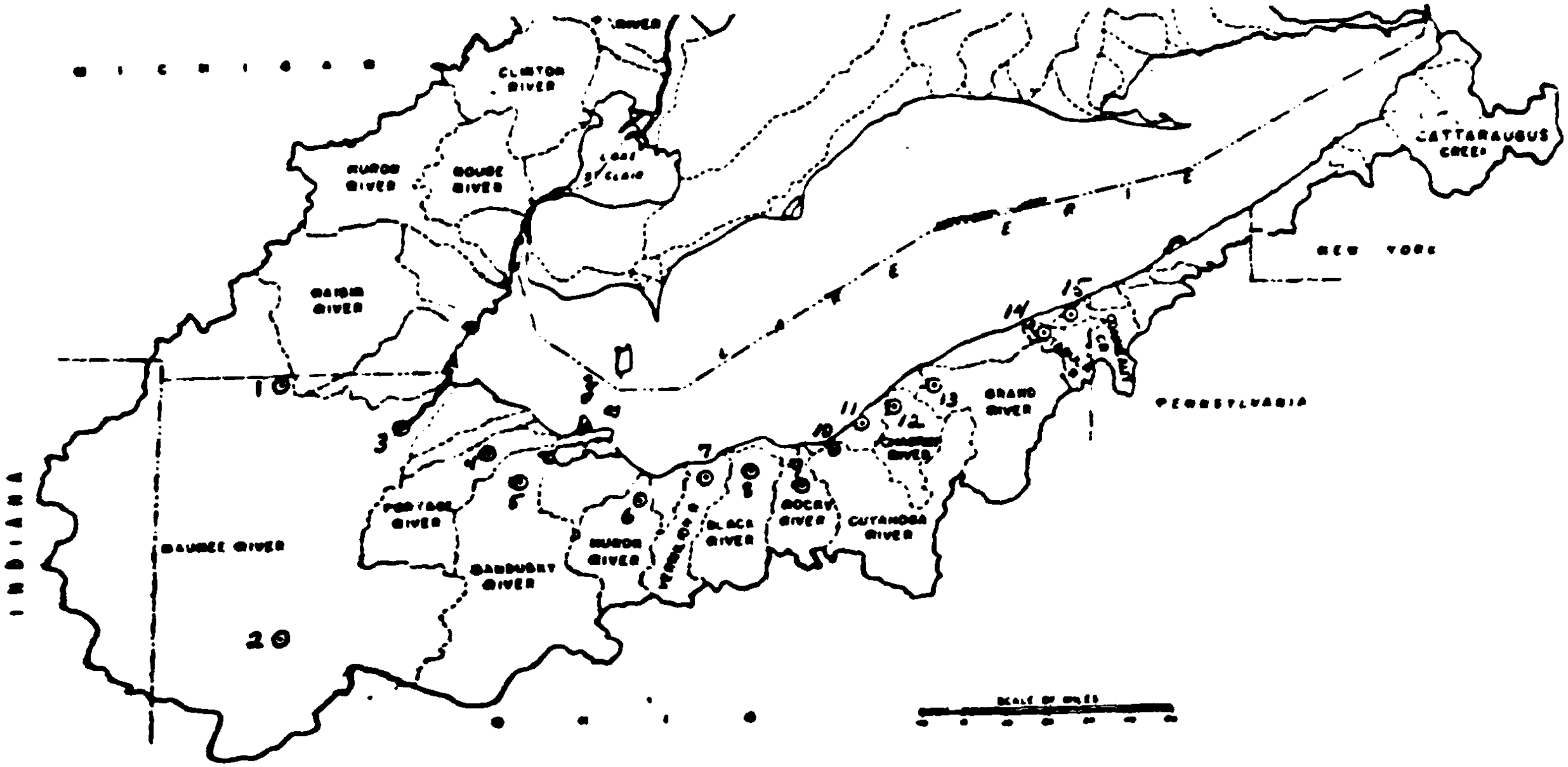


Figure 1. Sampling Stations in the Sandusky River Basin.



USGS Location Numbers

1. Bean Creek 04184500
2. Ottawa River at Allentown 04187500
3. Maumee River at Waterville 04193500
4. Portage River at Woodville 04195500
5. Sandusky River near Fremont 04198000
6. Huron River at Milan 04199000
7. Vermilion River near Vermilion 04199500
8. Black River below Elyria 04200550
9. Rocky River near Lakewood 04201555
10. Cuyahoga River at Cleveland 04208503
11. Euclid Creek near Euclid 04208690
12. Chagrin River at Willoughby 04209000
13. Grand River at Painesville 04212200
14. Ashtabula River near Ashtabula 04212700
15. Conneaut Creek at Conneaut 04213000

Figure 2. Sampling Stations in the Lake Erie Basin.

range of 10E-11 amps/mv and an attenuation of 1 on a 1 mv recorder.

The data for nitrates-nitrites and suspended solids listed in Tables 2, 3 and 5 were provided by the Heidelberg Water Quality Laboratory. The flow data in these tables was obtained from the U. S. Geological Survey.

QUALITY CONTROL

Of 12 reagent or method blanks prepared, only two showed detectable quantities of atrazine (0.1 ug/l). Five natural water samples were spiked with atrazine at several concentrations. The percent recoveries for these spikes are reported in Table 1.

Precision was monitored at three levels. Two consecutive samples were taken in the field and labeled as field replicates to study precision at the sampling level. A sample was split into portions labeled extraction replicates to monitor sample preparation precision. Injection replicates were made by analyzing an extract twice by GC in order to study instrumental precision. The percent difference data for these pairs of replicates are presented in Table 1.

Table 1. Quality Control Data - Atrazine

I. Percent recovery of spikes

Sample Concentration	ppb Added	% Recovery
7.2	5.0	134
5.3	10.0	91.2
8.5	10.0	98.0
2.6	10.0	100.0
10.4	25.0	110.0

II. Replicates

	Average Concentration (ug/ℓ)	% Difference
Field Replicates	14.2	16.9
	17.8	0.6
Extraction Replicates	9.2	3.0
	3.8	7.1
	4.0	10.8
	5.3	7.9
Injection Replicates	12.9	1.6
	10.6	1.9
	1.4	0.7

Table 2. Concentrations of atrazine, suspended solids, and nitrates-nitrites in waters taken from the Sandusky River and tributaries -- 1980.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
Bucyrus 04196000*			0519	1140	8.8	28.0	8.73
	111.6	13.7	0609	1115	12.2	360.4	11.79
	664.3	81.8	0616	1105	12.8	1586.8	7.57
	30.9	3.81	0630	1050	4.9	95.1	3.97
	71.0	8.74	0707	1027	4.6	240.6	5.81
	54.7	6.74	0714	1045	3.0	475.7	3.28
Melmore 04197100			0518-0519	Composite	33.8		
	320.4	23.5	0519	0950	33.4	91.7	26.
	176.6	13.0	0602	0855	45.7	314.4	13.87
	338.6	24.8	0609	0910	26.5	493.7	13.81
	48.3	3.54	0616	0910	10.4	148.7	5.60
	42.4	3.11	0630	0900	7.4	63.8	3.03
	31.0	2.27	0707	0850	10.1	314.0	7.95
	53.6	3.93	0714	0905	4.4	166.7	3.57
Mexico 04197000			0518-0519	Composite	9.0		
	1271.	18.0	0519	1245	11.3	84.6	12.73
	390.1	5.51	0602	1214	6.5	171.6	6.41
	5174	73.1	0606	0925	17.8	192.8	12.69
	1089.	15.4	0609	1255	10.5	210.9	9.78
	2001	28.3	0616	1255	14.9	1833.8	6.57
	65.0	0.918	0630	1200	3.3	49.2	3.03
	1231.	17.4	0707	1205	6.4	925.6	4.58
	482.2	6.81	0714	1230	4.8	399.6	4.33

Table 2 continued.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
Nevada 04196200			0518-0519	Com-posite	15.7		
	107.4	14.0	0519	1200	23.2	54.9	25.
			0602	1115	12.1	1344.	12.78
	70.0	9.14	0609	1150	15.3	376.5	12.69
	500.1	65.3	0616	1150	21.5	1945.	8.00
	15.7	2.05	0630	1115	3.6	224.3	4.03
	108.2	14.1	0707	1100	5.9	210.9	4.99
	20.8	2.72	0714	1115	2.5	224.3	2.42
Tindall 04198000			0518-0519	Com-posite	4.4		
	2392.	20.9	0519	1510	9.5	111.7	7.88
	1904.	16.6	0527	1505	23.4	444.0	12.88
	593.	5.18	0602	1440	8.7	133.4	7.93
	1904.	16.6	0609	1505	11.5	359.3	11.41
	1067.	9.33	0616	1520	6.5	152.1	8.03
	167.8	1.47	0630	1440	5.1	71.3	2.94
	2141	18.7	0707	1412	6.4	728.2	6.67
	143.7	1.26	0714	1435	3.2		
Upper Honey Creek 04197020			0518-0519	Com-posite	10.9		
			0519	1035	9.0	23.4	18.77
			0522-0523	Com-posite	1.1		
			0523-0524	Com-posite	1.0		
			0524-0525	Com-posite	13.3		
			0525-0526	Com-posite	21.1		
			0602	0940	12.8	882.8	14.58
			0609	1020	8.6	98.7	9.77
			0616	0955	20.7	632.2	13.79

Table 2 continued.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
			0630	0940	2.1	44.4	1.99
			0707	0935	4.0	96.3	5.72
			0714	0950	2.8	50.2	1.14
Wolf East 04197450			0518-0519	Composite	2.1		
	503.3	66.9	0519	1705	8.8	48.3	9.64
	269.1	35.8	0527	1540	7.6	164.5	13.58
	360.3	47.9	0602	1515	14.2	165.1	10.54
	452.1	60.1	0609	1535	5.8	171.6	12.21
	194.8	25.9	0616	1540	3.8	82.1	5.87
	115.4	15.3	0630	1500	4.7	51.3	5.99
	396.1	52.7	0707	1440	8.5	180.4	10.52
	213.2	28.4	0714	1500	2.6	77.7	3.57
Wolf West 04197300			0518-0519	Composite	6.4		
	99.8	16.5	0519	1730	4.0	26.3	18.78
			0524-0525	Composite	2.7		
	13.0	2.15	0527	1600	4.5	24.4	6.47
	78.1	12.9	0602	1540	5.0	124.2	9.67
	75.5	12.5	0609	1600	6.8	63.9	16.47
	28.7	4.74	0616	1600	2.4	118.2	6.51
	2.79	0.462	0630	1515	2.2	22.1	1.23
	58.4	9.64	0707	1500	5.5	65.8	10.09
	12.2	2.02	0714	1530	3.5	86.0	7.95

*USGS sampling location.

Table 3. Concentrations of atrazine, suspended solids, and nitrates-nitrites in waters taken from Bean Creek, Ottawa River and Rocky River -- 1980.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
Bean Creek 04184500*			0518-0520	Composite	6.7		
	384.8	20.4	0520	1407	3.2	71.2	2.40
	82.4	4.37	0528	1240	0.4	39.8	1.19
	507.9	26.9	0610	1335	6.4	135.2	2.19
	111.7	5.92	0617	1325	3.4	74.6	2.12
Ottawa River 04187500			0513-0520	Composite	5.2		
	87.3	5.97	0520	1050	5.3	16.4	15.86
	65.0	4.45	0528	1020	9.2	86.0	10.78
	99.8	6.83	0610	1030	2.3	32.9	10.46
	80.0	5.47	0617	1105	1.4	32.9	5.05
Rocky River (Valley City)			0521	1010	1.1	8.4	1.00
			0528	1030	0.4	6.3	2.73
			0611	1010	2.2	12.1	1.70
			0618	1015	2.8	11.2	1.42

*USGS sampling location.

Table 4. Concentrations of atrazine in waters taken from 13 Ohio streams flowing into Lake Erie -- 1980

Location	Date	Time	Atrazine (ug/ℓ)
Ashtabula River 04212700*	0605		2.9
Black River	0528	1130	1.9
04200550	0716	1400	6.8
	0716	1000	5.8
Chagrin River 04209000	0612	1200	0.8
Conneaut Creek 04213000	0605	1400	1.9
Cuyahoga River	0528	1145	0.2
04208503	0606	1200	0.1
	0612	1000	1.0
	0716	1430	0.2
Euclid Creek	0612	1100	0.1
04205690	0716	1800	0.1
Grand River	0604	1830	3.5
04212200	0612	1300	2.0
	0716	1300	1.8
Huron River	0528		1.4
04199000	0715		4.8
Maumee River	0520	1540	7.5
04193500	0528	1400	5.3
	0611	1200	8.5
04193490	0715	1400	3.7
Portage River	0528	1445	4.3
04195500	0715	1500	2.6
Rocky River	0528	1228	0.2
04201555	0716	1100	0.3
Sandusky River 04198000	0715		3.2
Vermilion River	0528	1344	2.3
04199500	0611	1700	23.2
	0715	1800	6.5

*USGS location number.

Table 5. Variation in concentrations of atrazine, suspended solids, and nitrates with time during a run off event for 4 Sandusky River stations.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
Melmore 04197100*	227.7	16.7	0527	0910	29.8	143.5	13.74
	202.1	14.8	0527	1300	25.7	238.8	13.27
	168.1	12.3	0527	1900	28.1	219.7	12.68
	150.3	11.0	0528	0100	19.2	234.7	11.76
	135.1	9.91	0528	0700	20.0	225.4	11.63
	120.5	8.84	0528	1300	20.6	204.5	11.00
	104.7	7.68	0528	1900	21.5	195.0	10.40
	96.7	7.10	0529	0100	21.5	150.7	10.03
	87.8	6.44	0529	0700	18.9	158.5	9.54
	82.9	6.08	0529	1300	19.3	147.8	9.07
	65.5	4.81	0530	1300	17.3	132.8	7.59
	86.6	6.35	0531	1300	17.0	157.1	6.90
	87.8	6.44	0601	1300	34.6	292.3	10.52
	161.5	11.8	0602	0700	50.0	274.0	13.10
	176.6	13.0	0602	0855	44.7	288.2	13.55
Mexico 04197000	651.8	9.21	0527	1245	14.1	270.7	12.87
	651.8	9.21	0527	1300	15.1	328.1	14.77
	390.1	5.51	0528	0100	14.7	194.6	14.59
	329.1	4.65	0528	0700	14.2	195.5	13.58
	278.0	3.93	0528	1300	17.0	193.4	12.98
	241.5	3.41	0528	1900	14.0	146.8	13.12
	210.0	2.97	0529	0100	14.2	143.9	13.14
	188.1	2.66	0529	0700	9.1	168.3	12.73
	174.3	2.46	0529	1300	13.1	135.9	12.41
	144.6	2.04	0530	0100	11.3	109.4	11.63
	127.7	1.80	0530	1300	9.2	125.3	10.80
	112.0	1.58	0531	0100	8.8	91.0	10.21
	105.4	1.49	0601	0100	7.0	91.5	8.93
	142.9	2.02	0602	0100	6.3	114.6	7.18
	395.6	5.59	0602	1214	6.6	193.0	6.58

Table 5 continued.

Location	Flow (ft^3/sec)	Flow/Area ($m^3 sec^{-1} ha^{-1}$)	Date	Time	Atrazine (ug/ℓ)	Suspended Solids (mg/ℓ)	NO_2+NO_3 (mg/ℓ N)
Tindall 04198000	1864	16.3	0527	1505	16.2	468.7	12.79
	1709	14.9	0527	1900	14.9	416.4	12.57
	1468	12.8	0528	0100	9.2	287.2	12.85
	1035	9.05	0528	1300	14.0	223.9	11.97
	908.1	7.94	0528	1900	12.4	205.1	12.28
	803.4	7.02	0529	0100	16.0	158.2	12.20
	706.3	6.17	0529	0700	15.2	145.7	12.38
	634.3	5.54	0529	1300	15.4	136.1	12.37
	587.3	5.13	0529	1900	14.9	112.1	12.30
	466.3	4.08	0530	1900	11.3	115.3	10.37
	474.4	4.15	0531	0700	10.0	122.4	10.35
	434.4	3.80	0531	1900	11.4	99.6	9.43
	466.3	4.08	0601	0700	7.5	89.4	8.06
	507.8	4.44	0602	0700	8.9	112.0	7.98
	587.3	5.13	0602	1440	8.5	142.5	7.93
Wolf West 04197300	13.0	2.15	0527	1600	3.8	21.5	6.31
	9.81	1.62	0528	1900	3.2	36.0	4.99
	8.77	1.45	0529	1900	2.3	35.9	4.34
	8.44	1.39	0531	1900	2.1	42.1	3.13
	8.44	1.39	0601	1900	2.6	49.7	2.17
	46.9	7.74	0602	1300	5.3	126.8	6.09
	78.1	12.9	0602	1540	3.9	131.7	9.71

*USGS sampling location.

RESULTS AND DISCUSSION

Seventy two samples from the Sandusky River and its tributaries were analyzed. The results are presented in Table 2. Data for suspended solids, nitrates-nitrites, and stream flow are also included. Atrazine was detected in all samples. Concentrations varied from 1.0 ug/l at Upper Honey Creek on May 23 to 45.7 ug/l at Melmore on June 2. Atrazine levels were generally higher at Melmore than at any other station. The only three values above 30 ug/l occurred there. Atrazine was present at levels above 20 ug/l in 12.5% of all samples, above 10 ug/l in 34.7% of the samples, and above 5 ug/l in 63.9% of the samples.

Sampling began on May 19 with the first rainfall after a prolonged dry spell of nearly a month during which most spring planting occurred. A rainy period ensued for about four weeks. Each station generally showed a gradual decline in atrazine concentration with time. However, there were major fluctuations which are correlated with the stage of the stream at the time of sampling. For almost every station, a dip in concentration occurred with the June 30 sample. Flows had been low throughout the basin for over a week previously. In some cases an even lower concentration was obtained on July 14. Although flows were somewhat elevated at this time, the levels of undegraded atrazine in the soil should have been reduced substantially due to both degradation and previous export during the eight weeks that had passed since the first runoff.

All samples other than those of June 30 were taken within several days of a rainfall. High atrazine levels were generally

observed to occur between May 19 and June 16. The date of the highest concentration varied with each station, because of variation in the time, intensity, and duration of rainfall throughout the basin. The flow data provide a relative indication of the intensity of the runoff event at the time of sampling and allow comparison of samples from a particular station. For comparison of samples from different stations the flow/area data is useful. The ratio of the flow to the basin area upstream from the site makes an approximate correction for stream size. In this way the same event at two sites can be compared, even though stream size and thus flow are very different.

For several stations, atrazine levels were studied at more frequent intervals during a runoff event to observe variation with time and to attempt correlation of atrazine concentrations with those of suspended solids and nitrate-nitrite and with the flow (Table 5). These data clearly show that the sampling time is a variable of major concern. Near times of peak flow, a change in sampling time of only a few hours makes a substantial difference in the atrazine concentration obtained. In Figures 3 and 4 the variation in atrazine with time is compared with flow, suspended solids, and nitrates-nitrites for two stations. Conductivity is substituted for flow in Figure 4, since flow data were not available for this station. The conductivity minimum indicates peak flow.

Figures 3 and 4 show that atrazine levels follow the levels of all three parameters. However, there is not enough evidence

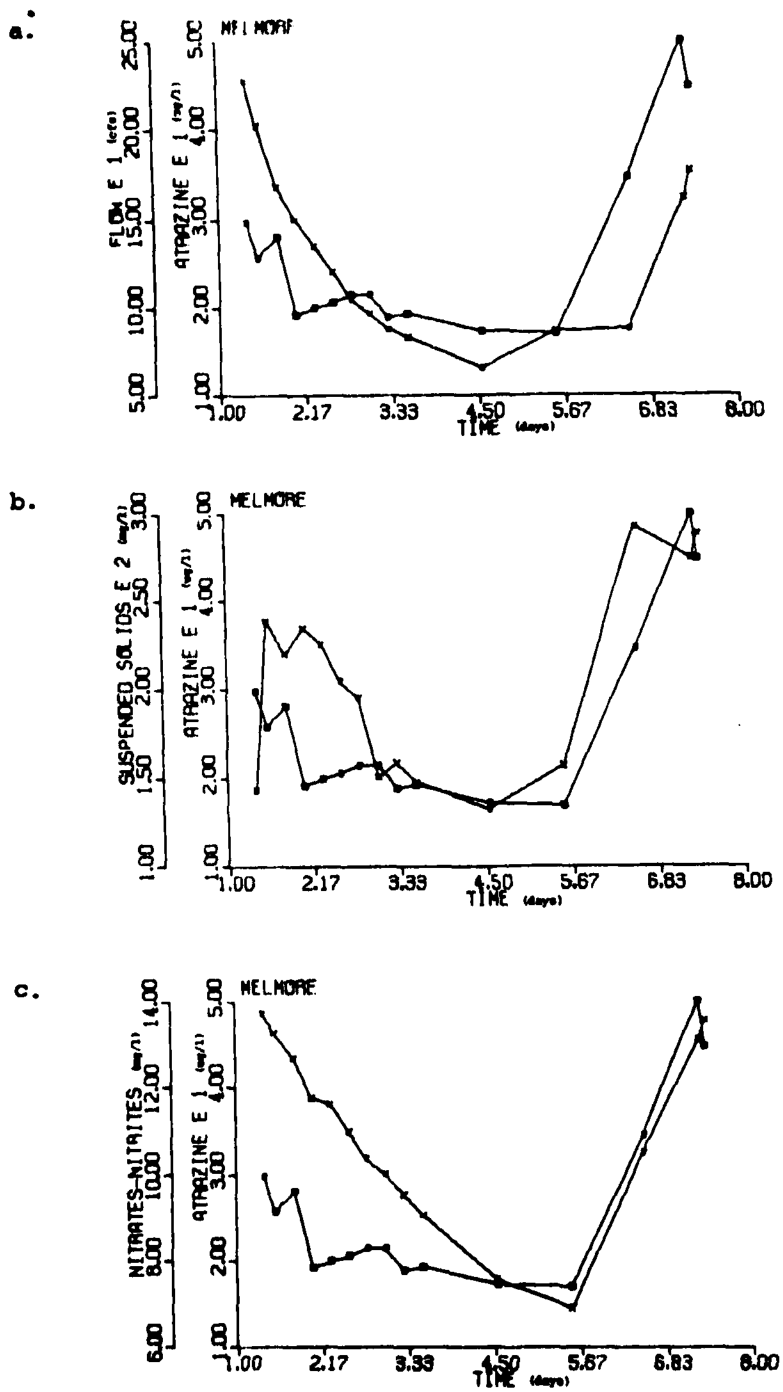


Figure 3. Time variation of atrazine at Melmore and time variation of: a. flow b. suspended solids and c. nitrates-nitrites (Table 5). Key: ☐ = atrazine x = other parameter.

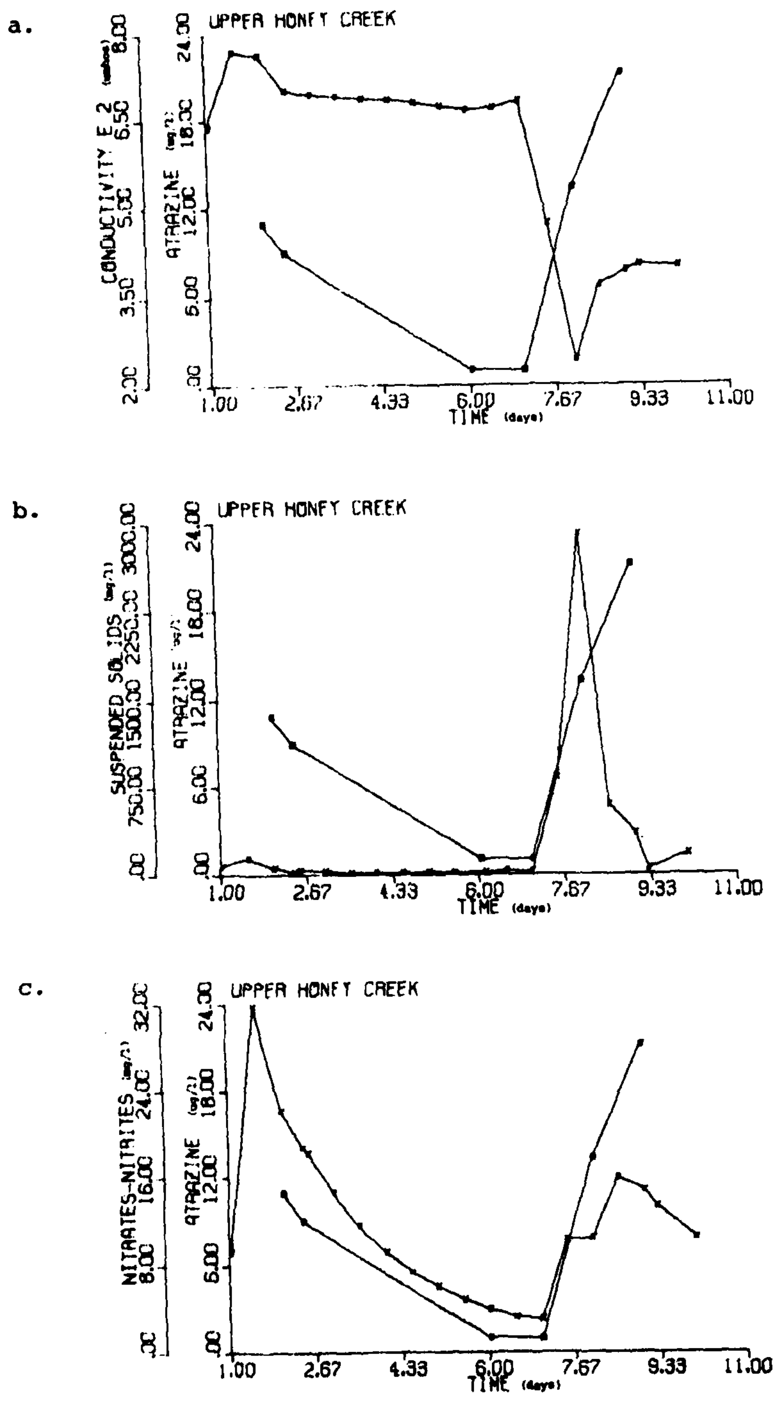


Figure 4. Time variation of atrazine at Upper Honey Creek and time variation of: a. conductivity b. suspended solids and c. nitrates-nitrites (Table 5). Key: ⊡ = atrazine x = other parameter.

to determine which parameter atrazine follows more closely, since in no case was the complete event enveloped by the samples chosen. Nevertheless, in both figures, suspended solids appear to have peaked while atrazine was still rising. A peak in suspended solids represents the presence of a large amount of runoff water, while a nitrate peak indicates some input from tile drainage and ground seepage. Thus, these data suggest that atrazine input from tile drainage may be significant. However, these data are by no means conclusive and further study is necessary. Muir and Baker (12) studied tile drain effluents for an entire season and found that 0.15% of the applied atrazine left the field via tile drainage as the parent compound or as a dealkylated metabolite. This amount becomes significant in view of the fact that total runoff losses of applied herbicides usually amount to less than 1% of the applied quantity (5, 14).

The linear correlation coefficients between atrazine and each of flow, suspended solids, and nitrates-nitrites were calculated for each Sandusky station. The best correlations generally were obtained with nitrates- nitrites. The Pearson product-moment correlation coefficient ranged from 0.61 to 0.83 for individual stations and was 0.63 for all Sandusky stations combined. A strictly linear relationship between atrazine and nitrates is not expected, because over a two month period the factors affecting the supply of the two parameters differ. The supply of atrazine in the soil is gradually being exhausted after application, while nitrates are replenished to some extent during the same period. Correlations over a shorter period of time,

such as the Table 5 data, might be expected to be higher. However, this is not demonstrated convincingly by this data. Nevertheless, the marked correlation obtained here does suggest that atrazine may follow the same mode of transport as nitrates, and further study is warranted. The correlation between atrazine and flow was also convincing for values from individual sites, but more variation was present. The coefficients ranged from 0.40 to 0.87. However, for all stations combined the correlation dipped to 0.21. This is not surprising in view of the fact that flow is not a concentration variable and varies for different sized streams under similar conditions. The ratio of flow to drainage area might be a better choice for this correlation. However, correlation with this ratio was only slightly higher (0.26) than that with flow. Correlations with suspended solids were generally somewhat lower and showed much variation between sites. The coefficients for individual sites ranged from 0.04 to 0.64 and the overall coefficient was 0.26. Suspended solids begin rising before the runoff water reaches the site due to resuspension of bottom sediments caused by the action of the advancing wave front. Thus, a weak correlation is not surprising.

Portions of two samples containing considerable suspended sediment were centrifuged before analysis. The total water samples and the centrifuged samples were analyzed and results compared. Identical results within the limits of the method precision were obtained. Thus the extraction procedure does not remove a significant amount of atrazine from the sediments and

the values reported in this work indicate atrazine levels in the water fraction of the total sample only. This result is not unexpected in view of the fact that Frank et al. (5) found no detectable residues of atrazine in 45 suspended solids samples collected in the Canadian Great Lakes Basin and extracted using procedures specific for soils.

Results for 15 Ohio streams in the Lake Erie basin are reported in Tables 3 and 4. Most of these samples were collected during periods of elevated flow. However, except for entries in Table 3, no attempt was made to correlate atrazine levels with other parameters. Atrazine was present at levels less than 1 ug/l in 23.3% of the samples, between 1.0 and 4.9 ug/l in 48.8%, between 5.0 and 9.9 ug/l in 25.6%, and above 10 ug/l in 2.3% of the samples. Atrazine levels in eastern streams were significantly lower than levels in the Sandusky basin. The average atrazine concentration in streams east of the Sandusky was 2.90 ug/l, while the average for all Sandusky sites was 9.71 ug/l. This marked difference is attributable to the relatively high agricultural acreage in the Sandusky basin.

Tiffin city water, which is taken from the Sandusky River, was also analyzed periodically (Table 6). Atrazine levels were similar to those found in the river, indicating that water treatment processes did little to remove atrazine. Richard et al. (13) studied finished water in several Iowa cities and found that water treatment processes were ineffective in removing atrazine regardless of whether an activated charcoal bed was used. Aged charcoal beds in some cases actually increased

Table 6. Concentration of atrazine in Tiffin city water -- 1980

Date	Atrazine (ug/ℓ)
0530	16.4
0616	7.2
0626	5.3
0701	3.3
0707	5.3

pesticide levels.

Several recent studies serve for comparison with the present work. Frank et al. (5) found a mean atrazine concentration of 3.3 ug/l in Canadian streams flowing into Lake Erie in mid-July 1977. The highest level detected was 26.0 ug/l. More than half of the 23 samples contained less than 1 ug/l. No mention was made of the flow levels of these streams at the time of sampling. In the present study the mean concentration for 18 samples taken in mid-July from the Sandusky and other streams was 3.1 ug/l. However, the values were not as widely distributed, with only 17% less than 1 ug/l.

In a study by Richard et al. (13), atrazine levels monitored periodically over the growing season for several streams in Iowa in 1974 showed similar patterns of decrease but were generally lower than the levels of the present study. Hormann et al. (7) studied triazine levels in Central European streams from spring 1976 to fall 1977. Sixty percent of all atrazine results were below 0.4 ug/l.

A survey of six southern Ontario watersheds over an entire growing season in 1974 was conducted by Frank et al. (6). The mean concentration for June was 5 ug/l, compared with 8.3 ug/l for the June samples of the present study and 10.6 ug/l for June samples of the Sandusky only. The highest concentration reported by Frank was 31.7 ug/l.

Dudley and Karr (4) detected no atrazine in samples taken from a watershed in northeastern Indiana. They attribute this result to the fact that sampling was done in late July after

fifteen days of low flow conditions.

The International Joint Commission in 1977 (8) defined water quality objectives for non-persistent organics such as the triazines as the 5% level of the median lethal concentration to the most sensitive local species at 96 hours. The IJC criteria for atrazine based on rainbow trout is 630 ug/l and 200 ug/l based on Daphnia magna. Thus it would appear that atrazine levels of the present study pose no immediate threat to animal life. However, effects of chronic exposure to low levels may be an issue. Macek et al. (9) studied the effect of chronic exposure to atrazine on reproduction and development of six animal species. The lower limits of maximum acceptable toxicant concentrations (MATC) ranged from 60 to 210 ug/l. In some species these levels resulted in reduced hatching success, larval mortality, developmental retardation, and similar problems. During the present study, atrazine levels approached these MATC concentrations only briefly, but did not exceed them.

It has already been demonstrated that the flow level of the stream and the time into a runoff event are major variables in an atrazine study. The purpose of the study should govern the choice of sampling time. If the total load of atrazine delivered by the stream is of interest, sampling must occur close to the peak flow. At this time both the concentration and flow are large, producing a very large load of atrazine. Timing the sample to coincide with the peak is important, since concentrations vary quickly near peak flows, making frequent sampling necessary. If the effect of long term exposure is to be

studied, measurement during low flow may be preferable, as this more accurately reflects the average concentrations experienced by the species of interest. Timing becomes much less critical, as concentrations vary only slowly during low flow.

If atrazine concentrations are to be correlated successfully with nitrate levels or other parameters, it may be necessary to focus attention on first order streams. The higher order streams studied here receive atrazine from a number of upstream sources with different patterns of atrazine application and rainfall, so that any correlations between atrazine and other parameters may be obscured or confused. The question concerning mode of transport may be more easily answered by direct sampling of field runoff and tile effluents.

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